



The quest for the elusive carbodiimide ion $\text{HN}=\text{C}=\text{NH}^+$ and its generation from ionized cyanamide by proton-transport catalysis

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ARTICLE INFO

Article history:

Received 24 June 2009

In final form 26 July 2009

Available online 29 July 2009

ABSTRACT

Tandem mass spectrometry based collision experiments and computational chemistry (CBS-QB3/APNO methods) indicate that the elusive carbodiimide ion $\text{HN}=\text{C}=\text{NH}^+$ is a stable species in the gas-phase. The ion is the most stable of the family of CH_2N_2^+ ions and a very high barrier (87 kcal mol^{-1}) separates it from its tautomer ionized cyanamide, $\text{H}_2\text{N}-\text{C}\equiv\text{N}^+$.

The computations also predict that, in the presence of a single H_2O molecule as the catalyst, the cyanamide ion isomerizes into the carbodiimide ion. Experiments on the ion–molecule reaction of $\text{H}_2\text{N}-\text{C}\equiv\text{N}^+$ and H_2O , a reaction of potential interest in astrochemistry, confirm this prediction.

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1. Introduction

Cyanamide $\text{H}_2\text{N}-\text{C}\equiv\text{N}$ (**1N**) is a key molecule in prebiotic synthesis [1–3] and one of a small group of molecules that are abundant in interstellar space [4]. IR spectroscopic studies of cyanamide in the gas-phase [5,6] indicate that its tautomer carbodiimide $\text{HN}=\text{C}=\text{NH}$ (**2N**) [7], also a molecule of considerable interest in astrochemistry, is present as a minor constituent. The equilibrium constant derived from these experiments [6] indicates that **1N** is more stable than **2N**, by $3.6 \text{ kcal mol}^{-1}$. However, as pointed out in the recent computational study of Tordini et al. [8], the equilibration of **1N** and **2N** is a bimolecular reaction: the intramolecular tautomerization involves a prohibitively high barrier of $\sim 90 \text{ kcal mol}^{-1}$. The study of Ref. [8] further predicts that the cooperative effect of only a few water molecules leads to a drastic reduction of the tautomerization barrier. Indeed, the subsequent matrix isolation experiments of Duvernay et al. [9,10] show that amorphous water–ice readily catalyzes the interconversion of cyanamide (**1N**) and carbodiimide (**2N**).

Other isomeric neutrals identified as stable species in the gas-phase are isocyanamide, $\text{H}_2\text{N}-\text{N}=\text{C}$ (**3N**) [11], nitrilimine, $\text{HC}=\text{N}=\text{NH}$ (**5N**) [12,13], as well as diazomethane, $\text{CH}_2\text{N}=\text{N}$ (**7N**), and its cyclic isomer diazirine, $\text{H}_2\text{C}-\text{N}=\text{N}$ (**8N**) [14]. Isodiazirine, $\text{HC}=\text{N}-\text{NH}$ (**4N**), has not (yet) been identified but, as corroborated by the computational results of our study, cyanamide clearly is the CH_2N_2 isomer of lowest energy.

The CBS-QB3 and APNO model chemistries [15,16] of the present study revealed that a different scenario obtains upon ionization of **1N** and **2N**. The carbodiimide ion $\text{HN}=\text{C}=\text{NH}^+$ (**2**) is more stable

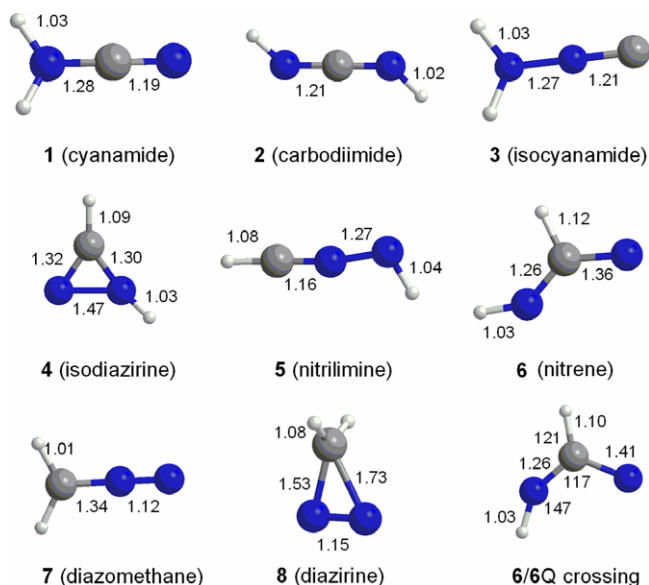
than the cyanamide ion $\text{H}_2\text{N}-\text{C}\equiv\text{N}^+$ (**1**). In fact, **2** represents the most stable member of the family of CH_2N_2^+ ions, whose optimized geometries are shown in Scheme 1. On the other hand, the intramolecular tautomerization of the ions by a 1,3-H shift faces the same high barrier (87 kcal mol^{-1}) as that for the neutrals. Thus, solitary ions **1** and **2** cannot interconvert.

This prompted us to explore whether their isomerization can be achieved by catalysis. Theory predicts, as will be discussed in Section 3.2, that a single molecule of water promotes the isomerization **1** \rightarrow **2**, by a process termed proton-transport catalysis [17]. Tandem mass spectrometry based experiments aimed to verify this prediction, viz. the ion–molecule reaction of **1** with H_2O described in the Section 2, rely upon an unambiguous assignment of the structure of the putative product ion **2**. In this context, the method of choice involves a comparative analysis of the high-energy collision-induced dissociation (CID) mass spectra [18] of the ion with the reference spectra of **1** and **2**. Reference CID mass spectra are readily available for **1**, as shown in the detailed study of Cacace et al. [19], and for several other isomers including **3** [20] and **5** [13], but the carbodiimide ion $\text{HN}=\text{C}=\text{NH}^+$ (**2**) has so far eluded experimental observation. Previous attempts to prepare the ion by either direct ionization of pyrolytically generated gaseous neutrals [20] or dissociative ionization of selected precursor molecules [21] failed to yield (pure) ions **2**.

This study describes the dissociation chemistry of $\text{H}_2\text{N}-\text{C}\equiv\text{N}^+$ (**1**) and $\text{HN}=\text{C}=\text{NH}^+$ (**2**), using the results of CID and CIDI (collision-induced dissociative ionization [18]) experiments in conjunction with a computational analysis of the isomerization behaviour of the ions. It will be shown that the elusive carbodiimide ion **2** is readily generated by dissociative ionization of 2-imidazolecarboxaldehyde [22] and also in the ion–molecule reaction of cyanamide ions **1** with H_2O .

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Scheme 1. Optimized geometries of the cyanamide ion **1** and its principal isomers obtained at the B3LYP/CBSB7 level of theory; bond lengths in Å. Also shown is the geometry of the crossing **6** → **6Q** discussed in Section 2.

2. Experimental and theoretical methods

The experiments on the solitary CH_2N_2 ions were performed on the VG Analytical ZAB-R mass spectrometer of BE_1E_2 geometry (B,

magnet; E, electric sector) under electron ionization conditions (70 eV) at accelerating voltages of 6–10 kV [23]. Metastable ion (MI) mass spectra were obtained in the second field-free-region (2ffr) and collision-induced dissociation (CID) mass spectra were obtained in the 2ffr and 3ffr using O_2 or He as the collision gas. Kinetic energy releases (KER) (corrected $T_{0.5}$ values) were obtained using standard procedures [18].

The NR-CID mass spectrum of Fig. 1b was obtained as described in Refs. [24,25]. The commercially available precursor molecules were introduced via a solids probe inlet.

The ion–molecule reaction of the cyanamide ion with H_2O was performed on the Mons AutoSpec 6F, a six-sector magnetic deflection instrument of EBEEBE geometry. The instrument is equipped with three cells (C_{1-3}) to realize high-energy collision-induced dissociations and an rf-only hexapole (HEX) reaction chamber for studies of associative ion–molecule reactions [26] so that the present configuration is: $\text{C}_1\text{E}_1\text{B}_1\text{C}_2\text{E}_2\text{-HEX-E}_3\text{B}_2\text{C}_3\text{E}_4$.

In brief, the experiment involves mass selection of a beam of m/z 42 cyanamide ions (8 keV) using the first three sectors. Next, the ions are decelerated to ~ 5 eV in front of the hexapole cell to optimize the yield of associative ion–molecule reactions with water vapour – at a pressure of $\sim 5 \times 10^{-4}$ mbar, as measured with a Pirani gauge located inside the cell. Following reacceleration to 8 keV, ions leaving the hexapole cell are mass analyzed by scanning the field of B_2 . Finally, the mass selected m/z 42 ions are subjected to collision-induced dissociation with O_2 in chamber C_3 , and their CID mass spectrum, see Fig. 1f, is obtained by scanning sector E_4 .

The calculations were performed using the GAUSSIAN 03 Rev. C.02 and D.01 suite of programs [27] on SHARCNET. Enthalpies of formation for the various ions and neutrals, see Tables 1 and 2,

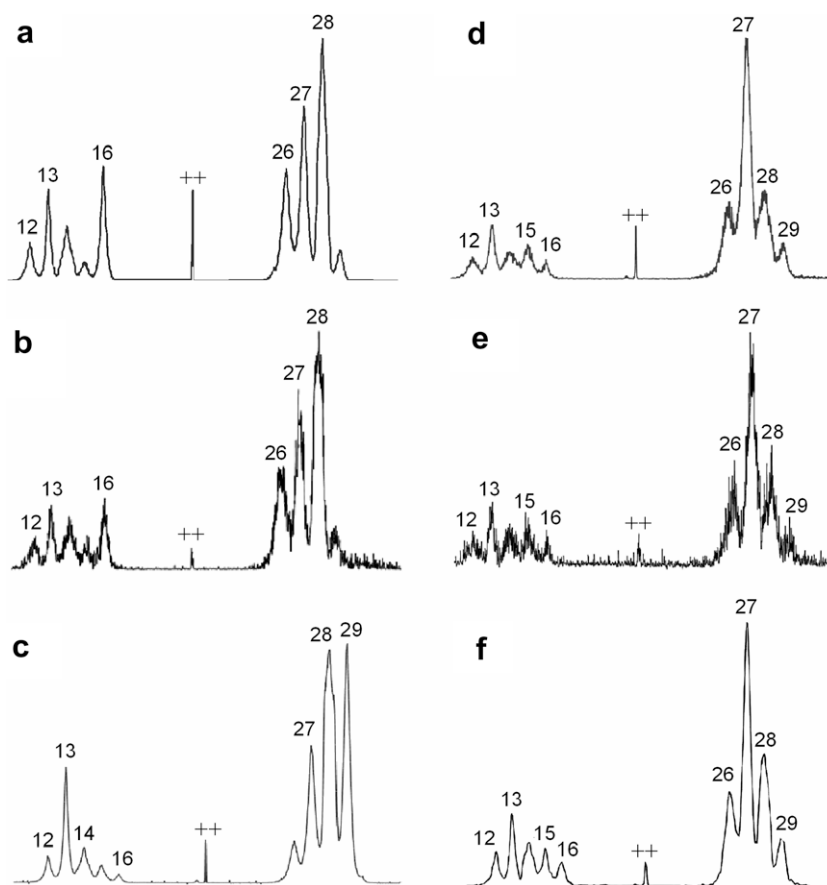


Fig. 1. (a) Partial CID spectrum; (b) NR-CID spectrum of cyanamide ions **1**; (c) partial CID spectrum of nitrilimine ions **5** generated from 1,3,4-triazole; (d) partial CID spectrum of carbodiimide ions **2** generated by the dissociative ionization of 2-imidazolecarboxaldehyde; (e) partial CID spectrum of the CIDI experiment on *N*-methylguanidine derived ions, see text and (f) partial CID spectrum of the m/z 42 ions generated in the ion–molecule reaction of ions **1** with H_2O .

Table 1
Energetic data^a derived from CBS-QB3 and CBS-APNO calculations of stable ions and connecting transition states involved in the dissociation chemistry of the cyanamide ion **1** and its water-catalyzed isomerization into the carbodiimide ion **2**.

Isomer		CBS-QB3 <i>E</i> (total) [0 K]	QB3 $\Delta_f H_{298}^0$	APNO $\Delta_f H_{298}^0$	Transition state	CBS-QB3 <i>E</i> (total) [0 K]	QB3 $\Delta_f H_{298}^0$	APNO $\Delta_f H_{298}^0$
H ₂ NC≡N ⁺	1	-148.17933	275.2	276.0	TS 1 → 3	-148.05169	352.5	354.9
HN=C=NH ⁺ (cis) ^b	2	-148.18646	271.1	270.9	TS 1 → 2	-148.04835	357.7	357.0
H ₂ NN=C ⁺	3	-148.11690	314.7	314.9	TS 2 → 4	-148.04561	359.4	361.1
HC=NNH ⁺	4	-148.11197	317.3	317.4	TS 2 → 6	-148.05699	351.9	^c
HC=N=NH ⁺	5	-148.14229	298.6	297.9	TS 3 → 4	-148.00993	381.3	379.9
HN=C(H)N ⁺	6	-148.05769	351.7	^c	TS 4 → 5	-148.06165	349.0	348.5
HN=C(H)N ⁺ (quartet)	6Q	-148.06545	346.7	346.5	TS 4 → 6	-148.06055	349.8	^c
H ₂ C=N=N ⁺	7	-148.18498	271.7	271.3	TS 7 → 8	-148.11187	317.6	^c
H ₂ CN=N ⁺	8	-148.11373	316.5	^c	TS 7 → 5	-148.03273	367.1	^c
					TS 6Q → <i>m/z</i> 28	-148.05751	351.7	351.8
H ₂ O...H ₂ NC≡N ⁺	H1	-224.55568	192.3	193.5	TS H1 → H2	-224.53377	205.3	204.9
H ₂ O...HN=C=NH ⁺	H2	-224.56694	185.2	186.4				

^a *E* (total) in Hartrees, all other components in kcal mol⁻¹.

^b CBS-QB3 predicts the ionic trans isomer to lie at 271.5 kcal mol⁻¹.

^c Geometry optimization could not be achieved.

Table 2
Energetic data^a from CBS-QB3 and CBS-APNO calculations for (i) various dissociation products of the CH₂N₂ ions of Schemes 2 and 3 and (ii) the neutral counterparts of the CH₂N₂ ions of Scheme 1.

Ion		CBS-QB3 <i>E</i> (total) [0 K]	QB3 $\Delta_f H_{298}^0$	APNO $\Delta_f H_{298}^0$	Neutral ^c	CBS-QB3 <i>E</i> (total) [0 K]	QB3 $\Delta_f H_{298}^0$	APNO $\Delta_f H_{298}^0$	
HNC≡N ⁺	<i>m/z</i> 41	-147.48071	349.3	348.7	H ₂ NC≡N	1N	-148.56529	33.0	33.6
H ₂ N=NH ⁺	<i>m/z</i> 31	-110.77246	229.3	229.5	HN=C=NH	2N	-148.56121	35.5	35.4 ^b
HN=NH ⁺	<i>m/z</i> 30	-110.13127	269.8	268.5	H ₂ NN=C	3N	-148.49446	77.5	77.9
HN ₂ ⁺	<i>m/z</i> 29	-109.57988	251.5	^d	HC=NNH	4N	-148.46572	95.2	96.2
HC=NH ⁺	<i>m/z</i> 28	-93.55430	226.4	226.8	HC=N=NH	5N	-148.47148	89.0	91.3
HC≡N ⁺	<i>m/z</i> 27	-93.78703	345.9	346.6	H ₂ C=N=N	7N	-148.51526	64.4	64.2
HN≡C ⁺	<i>m/z</i> 27	-92.82363	323.1	324.0	H ₂ CN=N	8N	-148.49755	75.1	75.6
NH ₂ ⁺	<i>m/z</i> 16	-55.38062	302.8	302.5	HN=C=N		-147.91569	76.2	76.9
NH ⁺	<i>m/z</i> 15	-54.65080	396.1	396.7	HN=C		-93.26616	45.5	46.5
CH ₂ ⁺	<i>m/z</i> 14	-38.69018	332.9	333.1	CN		-92.58753	106.6	106.4
H ₃ O ⁺	<i>m/z</i> 19	-76.59652	143.6	144.6	NH		-55.14448	86.1	86.2
CH ⁺	<i>m/z</i> 13	-38.02397	386.4	387.8	CH		-38.41267	142.5	142.6

^a *E* (total) in Hartrees, enthalpies are in kcal mol⁻¹.

^b A Weizmann-1 calculation yielded 35.0 kcal mol⁻¹.

^c The 298 K enthalpies for H, N, H₂O, and HCN (52.1, 113.0, -57.8 and 32.3 kcal mol⁻¹, respectively) were taken from Ref. [32].

^d Geometry optimization not achieved; from PA(N₂) = 118 kcal mol⁻¹ [30] a value of 248 kcal mol⁻¹ is derived.

were obtained from the CBS-QB3 [15] and CBS-APNO [16] model chemistries. The identity of local minima and connecting transition states (TS) was confirmed by frequency analysis. Unless stated otherwise, all enthalpies presented in the text and in the schemes (numbers in square brackets) refer to CBS-QB3 derived $\Delta_f H_{298}^0$ values in kcal mol⁻¹.

Since the dissociation of ion **6** of Scheme 2 into *m/z* 28 ions HC=NH⁺ (¹Σ_g⁺) by loss of N(⁴S), is spin-forbidden, the PESs were scanned in order to find a geometry where the doublet and quartet states are degenerate. Since the B3LYP/CBSB7 wave function optimization for the doublet state appeared to have multiple solutions (depending on the starting orbitals) leading to discontinuities in the PES, it appeared difficult to determine the lowest energy crossing point. Moreover, using the corresponding CBS-QB3 electronic energies leads to changes in the crossing point geometry, which are difficult to predict because no energy gradients are available for this composite method. Nevertheless, a continuous B3LYP/CBSB7 PES could be obtained by using starting orbitals obtained from a calculation for the neutral HN=C(H)N in its ³A' state, which does not suffer from the multiple solutions problem. The final crossing geometry shown in Scheme 1 was then obtained by trial and error. The CBS-QB3 electronic energies for this point differ by 0.5 kcal mol⁻¹. The electronic energy for the crossing (-148.09142) lies 4 kcal mol⁻¹ below TS **6Q** → *m/z* 28, so that it is not necessary to locate the minimum in the intersection of the

PESs. This TS, see Table 1, lies at 352 kcal mol⁻¹ so that the crossing is expected to lie at 348 kcal mol⁻¹.

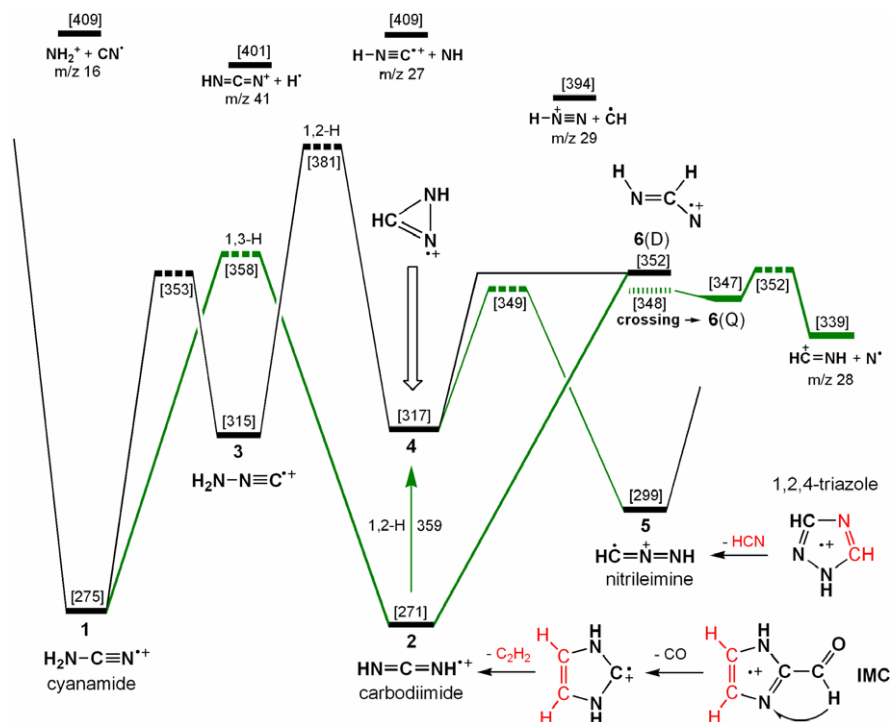
The two CBS model chemistries are expected to yield enthalpy values with chemical accuracy (±2 kcal mol⁻¹) [15,16]. However, several of the open-shell ions of Table 1 show (*S*²) values beyond the 'acceptable' range of ca. 5% of the theoretical value. The effect of spin-contamination on the accuracy is difficult to assess [28]. On the other hand, the potential energy diagrams of this study are not significantly different from those obtained at the B3LYP/CBSB7 level of theory, where spin-contamination is not an issue. Only TS **2** → **4** and geometries in the neighbourhood of ion **6** (TS **2** → **6**, TS **4** → **6** and the crossing) have large spin-contaminations in the DFT part of the calculation.

The complete set of computational results including the optimized geometries is available from the authors upon request.

3. Results and discussion

3.1. The characterization of CH₂N₂⁺ ions **1** and **2** using MI and CID mass spectrometry

In our analysis of the experimental results we will use the potential energy diagram of Scheme 2, which summarizes our calculations on the CH₂N₂⁺ system of ions, as a guide.



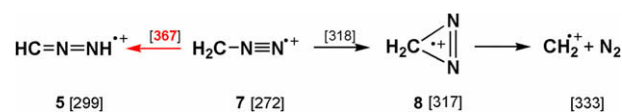
Scheme 2. Potential energy diagram for the loss of $N(^4S)$ from the cyanamide ion **1** and its principal isomers. The numbers in square brackets refer to CBS-QB3 derived $\Delta_f H_{298}^0$ values in kcal mol $^{-1}$.

It is seen that the cyanamide ion **1** lies in a deep potential well and that the barriers for isomerization into the carbodiimide ion **2** and the isocyanamide ion **3** are quite high. The carbodiimide ion **2**, which represents the global minimum on the PES, also lies in a deep well: communication by ring closure/opening with the stable ions **4** and **5** requires 90 kcal mol $^{-1}$.

The dissociation reaction of lowest energy requirement for these five isomeric ions, **1–5**, is a spin-forbidden process involving loss of $N(^4S)$ to yield $HC=NH^+$. As discussed in the experimental section, the crossing point for this reaction lies at ~ 348 kcal mol $^{-1}$ and involves the doublet and quartet states of nitrene ion **6**. In line with this, the reaction is associated with a significant reverse activation energy, which is reflected in the magnitude of the associated kinetic energy released (KER). For ion **1**, the KER in the formation of $N(^4S)$ and $HC=NH^+$, as measured from the width of the peak at half height is 500 meV (11 kcal mol $^{-1}$) [18,19]. We further note that the energy requirement for loss of $N(^4S)$ from ions **1**, **2**, **3**, **4** and **5** are very close. The dissociation characteristics of their *metastable* ions will therefore, be closely similar and indeed, for ions **3** [20] and **5** [13,29], a broad dish-shaped metastable peak has been reported for loss of $N(^4S)$. In this context we note that the cyclic isodiazirine ion **4** has been proposed to be generated from (substituted) azoles [29]. However, in a later NR study by Goldberg et al. [13], it was established that 1,2,4-triazole generates m/z 42 ions having the structure of the nitrilimine ion **5**, as indicated in Scheme 2. Thus, the MI spectrum cannot be used to differentiate ions **1–5**.

In contrast, see Scheme 3, the isomeric ions **7** and **8** are expected to behave differently: these ions could lose $N(^4S)$ via ion **5**, but the energy requirement for the associated 1,3-H shift greatly exceeds that calculated for the direct bond cleavage into $CH_2^+ + N_2$.

This is indeed borne out by the experimental observations: **7** and **8** both show a Gaussian-type metastable peak at m/z 14 (CH_2^+), albeit that the associated KERs are not the same [20]. Since all isomers lie in deep potential wells, their CID spectra may well

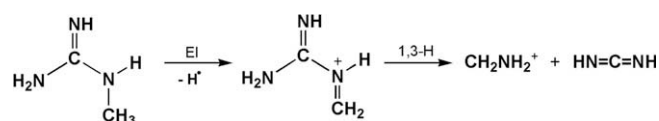


Scheme 3.

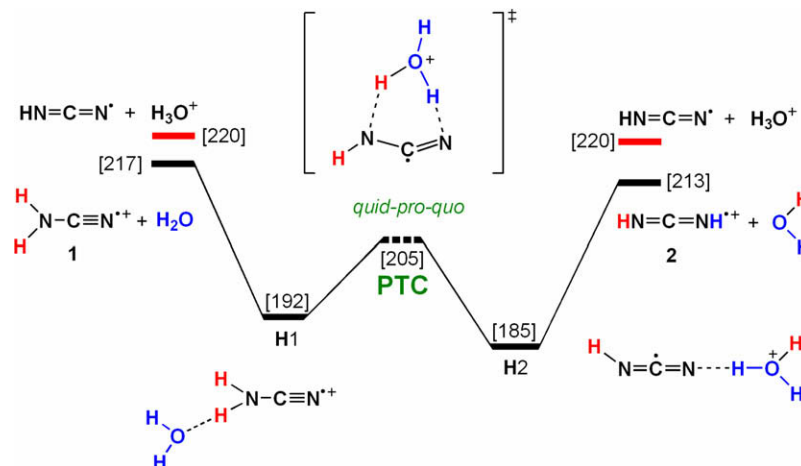
display peaks of structure diagnostic value [18]. The reported CID spectra all display an intense peak at m/z 41 for loss of H. This peak is not of structure diagnostic value but the weaker clusters of peaks in the m/z 26–30 and m/z 12–17 regions clearly are. For example, a unique peak at m/z 30 ($N_2H_2^+$), corresponding with the high-energy loss of C, easily differentiates the isocyanamide ion **3** from all other isomers [20]. In the same vein, the spectrum of the nitrilimine ion **5**, see Fig. 1c, is characterized by peaks at m/z 29 (N_2H^+) and m/z 13 (CH^+) [13,20], while a prominent m/z 14 (CH_2^+) peak characterizes the spectra of **7** and **8** [13,20].

The CID mass spectrum of **1** displays a structure diagnostic peak at m/z 16, indicative of the high-energy direct bond cleavage reaction $H_2N-C\equiv N^+ \rightarrow NH_2^+ + CN^-$. This is in line with the prediction of Scheme 2 that ions **1** retain their structure prior to metastable or collision-induced dissociation: the high barriers connecting ion **1** with the various CH_2N_2 isomers lie very close to the dissociation threshold for loss of $N(^4S)$.

To probe the isomeric and isobaric purity of the m/z 42 ions generated by electron ionization of the sublimed cyanamide sample [19], we have used the NR-CID technique described in Refs.



Scheme 4.



Scheme 5. Proton-transport catalysis (PTC) of the cyanamide ion **1**. The numbers in square brackets refer to CBS-QB3 derived $\Delta_f H_{298}^0$ values in kcal mol⁻¹.

[24,25]. The resulting spectrum of Fig. 1b is very close to that of Fig. 1a, thereby attesting to the purity of the m/z 42 ion beam.

As mentioned in the Section 1, 2-imidazolecarboxaldehyde (IMC) indeed yields carbodiimide ions **2**, by the consecutive loss of CO and C₂H₂, as depicted in Scheme 2.

The CID mass spectrum of these m/z 42 ions lacks the prominent structure diagnostic peaks in the CID mass spectra of ions **1**, **3**, **5** and **7**. Instead, Fig. 1d displays peaks at m/z 27 (HNC⁺) and m/z 15 (NH⁺), which support the carbodiimide ion structure assignment.

Complementary evidence for this structure assignment comes from a previous study [21] in which precursor molecules were examined that may lose *neutral* carbodiimide upon ionization. As indicated in Scheme 4, the prominent fragment ions at m/z 72 that result from loss of H⁺ from N-methylguanidine molecular ions, served to generate mass 42 neutrals for a collision-induced dissociative ionization (CIDI [18]) experiment.

The [M–H]⁺ ion shows a fairly intense peak at m/z 30 in its MI spectrum corresponding to a loss of mass 42. Indeed, a peak at m/z 42 dominates the CIDI mass spectrum of the m/z 72 ion. These m/z 42 ions, upon collisional activation, yield the spectrum of Fig. 1e, which is very close to that of Fig. 1d.

3.2. Proton-transport catalysis of the cyanamide radical cation

As discussed in the previous Section, theory predicts that the unassisted isomerization reaction of the cyanamide ion **1** into the more stable carbodiimide ion **2** does not occur spontaneously. This is corroborated by our experiments, which show that ions **1** and **2** have characteristically different CID spectra.

However, the proton-transport catalysis criterion [17] predicts that an efficient isomerization of ions **1** can be realized in an ion–molecule encounter complex with a neutral base, whose proton affinity (PA) lies between that of HN=C=N⁺ at HN and N, that is between 167 and 171 kcal mol⁻¹ (from the data in Tables 1 and 2). The water molecule may well be suitable as a catalyst because its PA, 165 kcal mol⁻¹ [30], lies only slightly below the above PA range.

The calculated potential energy diagram of Scheme 5 supports this contention. It shows that the interaction of a single water molecule with ion **1** leads to the stable hydrogen-bridged radical cation **H1**. Once formed, ions **H1** can easily overcome the isomerization barrier to generate the more stable species **H2**, which can then dissociate by loss of H₂O to yield ion **2**. The transition state associated

with the isomerization **H1** → **H2** is easily overcome because it lies lower than the combined enthalpies of ion **1** and H₂O.

Note that the proposed catalysis involves abstraction of a proton from the NH₂ moiety of the cyanamide ion by the H₂O molecule followed by back-donation of another proton from the protonated base. This type of proton-transport catalysis has been coined *quid-pro-quo* [31].

Experimental evidence for this reaction comes from the cyanamide (ion) – water (molecule) reaction in the hexapole cell of our tandem mass spectrometer, described in the Experimental. Fig. 1f shows the CID spectrum of the m/z 42 ions that have reacted with H₂O vapour in the hexapole reaction chamber. The observation that the spectrum of Fig. 1f is very close to that of Fig. 1d and e, demonstrates that water is an efficient catalyst for the isomerization of the cyanamide ion into its more stable carbodiimide tautomer.

Acknowledgements

J.K.T. and K.J.J. thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support, and SHARCNET for the computational resources. Alexander Imbault is gratefully acknowledged for his contributions to the computational component of this study. P.G. is grateful to the 'Fonds pour la Recherche Scientifique' (FRS-FNRS) for financial support in the acquisition of the Waters Autospec 6F and for continuing support.

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